



Three purine-containing metal complexes with discrete binuclear and polymeric chain motifs: Synthesis, crystal structure and luminescence



Zheng-Yu Liu^a, Hui-Ming Dong^a, Xiu-Guang Wang^a, Xiao-Jun Zhao^{a,b,*}, En-Cui Yang^{a,*}

^a College of Chemistry, Key Laboratory of Inorganic–Organic Hybrid Functional Material Chemistry, Ministry of Education, Tianjin Key Laboratory of Structure and Performance for Functional Molecules, Tianjin Normal University, Tianjin 300387, PR China

^b Synergetic Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300071, PR China

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ABSTRACT

To investigate the influences of exocyclic substituent of purine base on the coordination and recognition behavior, three new purine-based inner-sphere metal complexes, $[\text{Cd}_2(\text{H}_2\text{ade})_2(\text{H}_2\text{O})_4(\text{btc})_2] \cdot 4\text{H}_2\text{O}$ (**1**), $[\text{Cd}_2(\text{Hhyp})_2(\text{H}_2\text{O})_4(\text{Hbtc})_2] \cdot 4\text{H}_2\text{O}$ (**2**), and $[\text{Cd}(\text{H}_2\text{dap})(\text{H}_2\text{O})_2(\text{btc})]_n$ (**3**) (Hade = adenine, Hhyp = hypoxanthine, Hdap = 2,6-diaminopurine, and H_3btc = 1,2,4-benzenetricarboxylic acid), were hydrothermally synthesized and structurally characterized. The former two complexes with monodentate $\text{H}_2(\text{N}1, \text{N}9)\text{ade}^+$ cation (for **1**) and $\text{H}(\text{N}1, \text{N}7)\text{hyp}$ molecule (for **2**) are centrosymmetric binuclear entities aggregated by a pair of tricarboxylate ligand. In contrast, **3** bearing a cationic $\text{H}_2(\text{N}1, \text{N}9)\text{dap}^+$ ligand has a polymeric one-dimensional helical chain extended by btc^{3-} connectors. The side group of the purine can significantly dominate and stabilize the supramolecular network by different H-bonding recognition patterns. Additionally, these three samples with considerable thermal stability display strong emissions originated from ligand-based electron transfer, suggesting their potential application as luminescent materials.

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1. Introduction

Metal complexes with nucleobase as organic ligand have recently received widespread attention due to their structural diversity [1,2] and promising applications in molecular recognition [3,4], magnetism [5], luminescence [6], catalysis [7], molecular electronics [8], and gas absorption [9,10]. Very recently, Verma and his co-workers have successfully constructed a series of adenine (Hade) and its diverse derivatives-containing coordination frameworks, revealing the coordination behavior of adenine and metal ion, the crystal patterns of the metal–Hade coordination architectures on the graphite and other surfaces, as well as the catalysis performance of the adenine polymers [6,7]. By incorporating a series of secondary polycarboxylate coligands into ternary self-assembly systems under hydrothermal conditions, we also obtained some unprecedented cation binding modes of Hade, 2,6-diaminopurine (Hdap), and hypoxanthine (Hhyp) nucleobases

with transition metal ions [11–14]. However, the influences of the exocyclic side group on the binding mode and H-bonding pattern have been scarcely explored by far. As our continuous investigations along this line [11–14], herein, three purine bases modified by different substituents (single and double amino group for Hade and Hdap, as well as an oxo-moiety for Hhyp) were selected to self-assemble with $\text{Cd}(\text{II})$ ion (a soft Pearson acid) and 1,2,4-benzenetricarboxylic acid (H_3btc). Obviously, our particular purpose is focused on the roles of the amino- or oxo-segment of the purine base on the binding and recognition behavior of the resulting metal–nucleobase complexes. As a result, three new nucleobase-containing inner-sphere metal complexes including two discrete binuclear entities and one polymeric helical chain, $[\text{Cd}_2(\text{H}_2\text{ade})_2(\text{H}_2\text{O})_4(\text{btc})_2] \cdot 4\text{H}_2\text{O}$ (**1**), $[\text{Cd}_2(\text{Hhyp})_2(\text{H}_2\text{O})_4(\text{Hbtc})_2] \cdot 4\text{H}_2\text{O}$ (**2**), and $[\text{Cd}(\text{H}_2\text{dap})(\text{H}_2\text{O})_2(\text{btc})]_n$ (**3**), were successfully obtained under the optimized hydrothermal conditions. Structural analysis suggests that the coordination frameworks of the targeted nucleobase metal complexes are significantly manipulated by the aromatic tricarboxylate ligand with variable deprotonation extent. In contrast, the three purines can act as monodentate ligands to complete metal coordination sphere and to further direct and reinforce the supramolecular networks by differently hydrogen-bonding recognition patterns. Additionally, these complexes with considerable higher thermal stability can display strong fluorescent emissions originated from intra-/inter-ligand charge transfer.

* Corresponding authors. Address: College of Chemistry, Key Laboratory of Inorganic–Organic Hybrid Functional Material Chemistry, Ministry of Education, Tianjin Key Laboratory of Structure and Performance for Functional Molecules, Tianjin Normal University, Tianjin 300387, PR China. Fax: +86 022 23766556 (X.-J. Zhao).

E-mail addresses: xiaojun_zhao15@163.com (X.-J. Zhao), encui_yang@163.com (E.-C. Yang).

2. Experimental

2.1. Reagents and instruments

All the starting materials were commercially purchased (Hade, Hhyp, Hdap, and H₃btc were from Acros and other analytical-grade reagents were from Tianjin Chemical Reagent Factory) and used as received without further purification. Doubly deionized water was used for the conventional synthesis. Fourier transform (FT) IR spectra (KBr pellets) were taken on an Avatar-370 (Nicolet) spectrometer. Elemental analyses for C, H, and N were performed on a CE-440 (Leemanlabs) analyzer. TG-DTA experiments were carried out on a Shimadzu simultaneous DTG-60A thermal analysis instrument with a heating rate of 8 °C·min⁻¹ from room temperature to 800 °C under N₂ atmosphere (flow rate 10.0 mL·min⁻¹). Powder X-ray diffraction (PXRD) patterns were obtained using a Bruker D8 ADVANCE diffractometer at 40 kV and 40 mA for Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$), with a scan speed of 0.1 s per step and a step size of 0.01° in 2 θ . The simulated PXRD patterns were calculated using single-crystal X-ray diffraction data and processed by the free MERCURY v1.4 program provided by the Cambridge Crystallographic Data Center. Fluorescence spectra of the polycrystalline samples were performed on a Fluorolog-3 fluorescence spectrophotometer from Horiba Jobin Yvon at room temperature.

2.2. Synthesis of [Cd₂(H₂ade)₂(H₂O)₄(btc)₂]·4H₂O (1)

A mixture containing Cd(NO₃)₂·6H₂O (61.6 mg, 0.2 mmol), Hade (27.0 mg, 0.2 mmol), and H₃btc (21.0 mg, 0.1 mmol) was dissolved in doubly deionized water (10.0 mL) and the initial pH value of the reaction mixture was adjusted to ca. 6 by triethylamine. The resulting mixture was then transferred into a Parr Teflon-lined stainless steel vessel (23.0 mL) and was heated at 100 °C for 72 h under autogenous pressure. After the mixture was cooled to room temperature at a rate of 1 °C h⁻¹, colorless block-shaped crystals suitable for X-ray diffraction analysis were obtained directly and separated manually. Yield: 39.0% based on H₃btc. *Anal.* Calc. for C₁₄H₁₇CdN₅O₁₀: C, 31.86; H, 3.25; N, 13.27. Found: C, 31.69; H, 3.49; N, 13.34%. FT-IR (cm⁻¹): 3367(br), 3303(br), 3141(w), 1701(s), 1575(s), 1545(s), 1489(m), 1378(s), 1239(m), 1127(m), 1074(w), 1025(w), 953(w), 876(w), 833(w), 774(w), 741(w), 622(m), 511(m).

2.3. Synthesis of [Cd₂(Hhyp)₂(H₂O)₄(Hbtc)₂]·4H₂O (2)

A mixture containing Cd(NO₃)₂·6H₂O (61.6 mg, 0.2 mmol), Hhyp (37.2 mg, 0.2 mmol), and H₃btc (21.0 mg, 0.1 mmol) was dissolved in doubly deionized water (10.0 mL) and the initial pH value of the reaction mixture was adjusted to ca. 6 by triethylamine. The mixture was then transferred into a Parr Teflon-lined stainless steel vessel (23.0 mL) and heated at 120 °C for 72 h under autogenous pressure. After the mixture was cooled to room temperature at a rate of 1.3 °C h⁻¹, colorless block-shaped crystals suitable for X-ray diffraction analysis were obtained. Yield: 15.5% based on H₃btc. *Anal.* Calc. for C₁₄H₁₆CdN₄O₁₁: C, 31.81; H, 3.05; N, 10.60. Found: C, 31.74; H, 3.16; N, 10.77%. FT-IR (cm⁻¹): 3437(br), 3148(w), 1686(vs), 1551(s), 1491(m), 1417(s), 1396(s), 1372(s), 1309(m), 1252(w), 1224(w), 1166(w), 1124(w), 1097(w), 1075(w), 965(w), 903(w), 875(w), 845(w), 801(w), 769(w), 711(w), 669(w), 621(w), 568(w), 532(w).

2.4. Synthesis of [Cd(H₂dap)(H₂O)₂(btc)]_n (3)

A mixture containing Cd(NO₃)₂·6H₂O (61.6 mg, 0.2 mmol), Hdap (15.0 mg, 0.1 mmol), and H₃btc (21.0 mg, 0.1 mmol) was

dissolved in doubly deionized water (10.0 mL) and the initial pH value was adjusted to ca. 6 by triethylamine. The mixture was then transferred into a Parr Teflon-lined stainless steel vessel (23.0 mL) and was heated at 100 °C for 72 h under autogenous pressure. After the mixture was cooled to room temperature at a rate of 3 °C h⁻¹, colorless block-shaped crystals suitable for X-ray diffraction analysis were obtained directly and separated manually. Yield: 31.0% based on H₃btc. *Anal.* Calc. for C₁₄H₁₄CdN₆O₈: C, 33.19; H, 2.78; N, 16.59. Found: C, 33.13; H, 2.86; N, 16.66%. FT-IR (cm⁻¹): 3332(w), 3275(w), 3139(w), 1706(s), 1667(s), 1556(s), 1537(s), 1418(s), 1365(vs), 1172(w), 1134(w), 1076(w), 1011(w), 962(m), 861(m), 816(m), 789(w), 772(m), 719(m), 662(w), 625(w), 593(w), 531(w), 495(m).

2.5. X-ray crystallography

Diffraction intensities for **1–3** were collected on a Bruker APEX-II QUAZAR diffractometer equipped with graphite-monochromated Mo K α radiation with a radiation wavelength of 0.71073 Å by using the φ - ω scan technique at 296 K. There was no evidence of crystal decay during data collection. Semiempirical absorption corrections were applied (SADABS), and the program SAINT was used for integration of the diffraction profiles [15]. The structures were solved by direct methods and refined with the full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs [16]. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically. The H atoms of the water molecules were located from difference maps and refined with isotropic temperature factors. Further crystallographic data and structural refinement details were summarized in Table 1. Selected bond lengths and angles were listed in Tables 2–4. And the hydrogen-bonding parameters were given in Table 5.

3. Results and discussion

3.1. Synthesis and IR spectra

Colorless block-shaped crystals of **1–3** were hydrothermally prepared by the reactions of Cd^{II} salt, H₃btc, and different nucleobases in a slightly weak acidic medium, confirming that the hydrothermal approach is highly efficient for the self-assembly of the nucleobase-based inner-sphere metal complexes [11–14]. The pH value controlled by triethylamine and reaction temperature are found to be important factors for the successful preparation/crystallization of the three targeted complexes. The weak acidic medium plays importantly dual roles on the deprotonation of nucleobases and aromatic tricarboxylic acid as well as the proton tautomerization of the purine bases. Relatively lower reaction temperature is required for the higher-yield preparation of **1** and **3** with single and double amino group modified purine bases. In contrast, complex **2** with neutral Hhyp nucleobase can only be fabricated in a lower yield through relatively higher reaction temperature and prolonged reaction time, which is probably due to the poor solubility of Hhyp nucleobase.

In the IR spectra, strong broad bands beyond 3275 cm⁻¹ for **1–3** should be ascribed to the stretching vibrations of O–H and/or N–H, suggesting the presence of amino group of the nucleobase and water molecule. The very strong peak located at 1686 cm⁻¹ in **2** could be assigned to the overlap of undeprotonated carboxylic and exocyclic oxo-group. In contrast, strong absorptions located at ca. 1700 cm⁻¹ in both **1** and **3** are likely to be the hydrogen bonds associated with the deprotonated carboxylate and the amino group of purine base [17]. The asymmetric and symmetric stretching bands for the carboxylate groups are

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